ISOTOPE EXCHANGE BETWEEN A SOLID

AND A GAS

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ISOTOPE EXCHANGE BETWEEN A SOLID BODY AND A GAS

/The following is a translation of an
article written by S. N. Oziraner in Problemy
Kinetiki i Kataliza (Problems of Kinetics and
Catalysis), pages 267-273./

A study of the isotope exchange between a solid bo-
dy and a gas plays an important role in explaining the
chemical and physical mechanism of processes taking place
in heterogeneous systems. In the first place it concerns
such processes as absorption and heterogeneous catalysis.

In numerous investigations of the isotope exchange
in heterogeneous systems (see for instance, the detailed
survey of Val and Bonner), the summary effect of the ex-
change is examined without attempting to fix the limits
of the two independent stages of the process -- the ex-
change on the surface of the phase division, and the
diffusion inside the solid body. At the same time, as a
rule, one of the stages is accepted as a controlling
agent of the summary exchange process, often without suf-
ficient foundation to warrant it. In the presence of com-
mensurate velocities of both stages of the isotope ex-
change, such an interpretation of the results cannot be
considered satisfactory. On the strength of this, it is
of interest to find criteria that allow fixing the limits
of both stages of the isotope exchange process and, thro-
ugh them, determining the true values of the velocity-ex-
change constant on the boundary line of the phase division
and the value of the self-diffusion coefficient.

The present investigation is devoted to a search
for these criteria and to an experimental verification of
results obtained from calculation.

Let us examine the following conditions of the iso-
tope exchange process between a gas and a solid body. Let
us assume that a solid body containing a marked radioactive
isotope is deposited in the form of a thin layer. If the
thickness of the layer is small so that the absorption of
the measured radiation can be neglected, the registered

radioactivity of the layer is proportional to the number of marked atoms contained in the solid body at a given moment of time.

For simplification of the calculation, we shall assume that the solid body consists of separate particles in the shape of little spheres with an average radius r_0 and that it is an isotope. At the beginning, the marked atoms are distributed in the particle uniformly and their concentration in the entire volume is $n = n_0$.

Then the total quantity of the marked atoms in the entire underlying layer will be:

$$N = m \frac{4}{3} \pi r_0^3 n_0, \qquad (1)$$

where m — is the quantity of particles.

Let the exchange velocity on the boundary of the division of a unit area be determined by the value of R, depending on the concentration of exchanging gas c and the temperature T; that is, $R = R(c, T)$ — the observed constant of the velocity exchange. The quantity of the marked atoms migrating into the gaseous phase in a unit of time from one unit of area at $t = 0$ will be:

$$-\frac{dn}{dt} = Rn = Rn_0 \qquad (2)$$

and for all particles of the solid body:

$$-\frac{dN}{dt} = Rn_0 S = Rn_0 4\pi r_0^2 m. \qquad (3)$$

From (1) and (3) follows that:

$$-\frac{dN}{dt} = \frac{3R}{r_0} N \qquad (4)$$

or:

$$\frac{N}{N_0} = a = e^{-\frac{3R}{r_0} t}. \qquad (5)$$

Therefore, the slope of the tangent to the curve line $\ln a - t$

at the point $t=0$ determines the value $\boxed{\frac{3R}{r_0}}$. The value a— a portion of the unexchanged atoms — is equal to the ratio of the radioactivity of the layer at the given moment of time and at the initial moment.

For $t>0$ the change in the concentration of the reactive atoms n can be determined by solving an equation of diffusion:

$$\frac{\partial n}{\partial t} = D\Delta n, \tag{6}$$

where Δ—is a Laplace operator.

For the isotope solid body consisting of particles — little spheres — equation (6) can be expressed in the following form:

$$\frac{\partial n}{\partial t} = D\left(r\frac{\partial^2 n}{\partial r^2} + 2\frac{\partial n}{\partial r}\right) \tag{7}$$

with limiting conditions

$$\text{for } r=r_0; \quad -D\frac{\partial n}{\partial r} = Rn \tag{8}$$

and initial conditions

$$\text{for } t=0 \quad \begin{array}{l} n=n_0 \text{ для } 0<r<r_0 \\ n=0 \text{ для } r>r_0 \end{array} \tag{9}$$

This problem is analogous to a problem of the cooling velocity of a uniformly heated sphere in a space with a temperature equal to zero, and it has the following solution:

$$n(r,\ t) = \sum_{i=1}^{i=\infty}\left(A_i \frac{\sin\lambda_i \frac{R}{D}r}{\frac{R}{D}r} + B_i \frac{\cos\lambda_i \frac{R}{D}r}{\frac{R}{D}r}\right)e^{-\lambda_i^2\frac{R^2}{D}t} \tag{10}$$

From the condition of symmetry according to a beam, $B_i=0$. In addition, for a sufficiently long duration of time, the series quickly diminishes and therefore it is only necessary

to consider the first term:

$$n(r, t) = A \frac{\sin \lambda \frac{R}{D} r}{\frac{R}{D} r} e^{-\lambda^2 \frac{R^2}{D} t}. \tag{11}$$

Parameter λ can be found from the limiting conditions (8) by substituting solutions (11)

$$\operatorname{ctg} \frac{R r_0}{D} = \frac{1}{\lambda} \left(\frac{D}{R r_0} - 1 \right). \tag{12}$$

Transposing the last equation, we have

$$\lambda = \frac{D}{R r_0} \varphi, \tag{13}$$

where φ is determined by the relationship

$$1 - \varphi \operatorname{ctg} \varphi = \frac{R r_0}{D}. \tag{14}$$

Substituting (13) into (11), we finally have:

$$n(r, t) = A \frac{\sin \frac{r}{r_0} \varphi}{\frac{R}{r_0} r} e^{-\varphi^2 \frac{D}{r_0^2} t}. \tag{15}$$

Integrating expression (15) for r from 0 to r_0, we have:

$$\alpha = \frac{N}{N_0} = \operatorname{const}(\varphi) e^{-\varphi^2 \frac{D}{r_0^2} t}. \tag{16}$$

Therefore, for sufficiently great periods of time, the curve $\ln \alpha - t$ straightens and its slope is determined by the value $\varphi^2 \frac{D}{r_0^2}$.

If we designate the tangent of the angle of the slope $\ln \alpha - t$ by $t = 0$

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$$z = \frac{3R}{r_0},\qquad(17)$$

and the straight part of the curve for large t by

$$y = \varphi^2 \frac{D}{r_0^2},\qquad(18)$$

then from the equalities (14), (17), (18) we have:

$$\frac{z}{y} = 3\left(\frac{1 - \varphi\,\mathrm{ctg}\,\varphi}{\varphi^2}\right) = 3f(\varphi).\qquad(19)$$

According to the graph of the function $f(\varphi)$ we find the value φ.

Therefore, from the experimental data, it is possible to find the values

$$\frac{R}{r_0} \quad \text{and} \quad \frac{D}{r_0^2}.$$

If the mean statistical measurements of the solid body particles are determined by an independent method, the values R and D, -- the observed velocity constant of the isotope exchange reaction on the surface, and the coefficient of self-diffusion -- can be found.
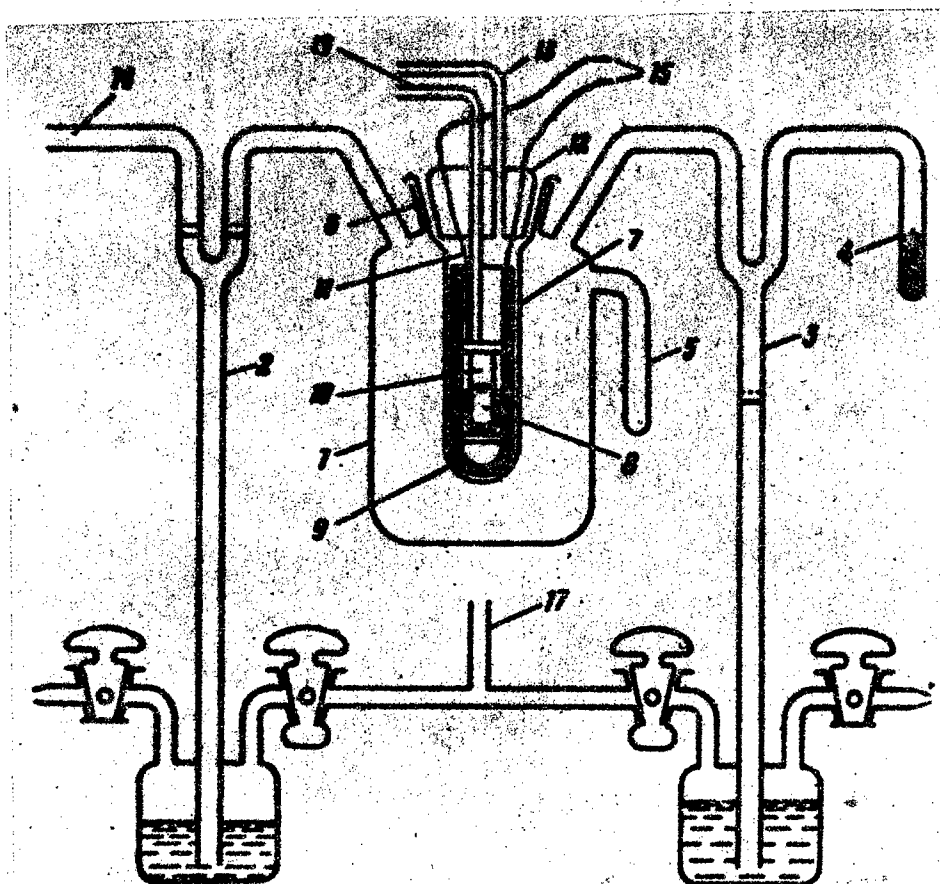
Fig. 1. Reaction part of the installation.
1-reaction container; 2,3 - mercury stoppers; 4 - tubing
with crystalline iodine; 5 - an extension for freezing
out; 6 - ground neck for stopper; 7 - beaker; 8 - window;
9 - lead shield; 10 - Geiger-Müller counter; 11 - tubing
for filling the counter; 12 - stopper; 13 - tube for eva-
cuation of the beaker; 14 - branch pipe to mercury pumps;
15 - conducting leads to intensifier; 16 - to installa-
tion for filling the counter; 17 - to vacuum.

Experimental confirmation of the presented calcula-
tions is shown in an example of a kinetics study of the
isotope exchange between solid iodites and gaseous iodine.
Experiments were conducted with an installation a
diagram of which is shown in Fig. 1.
The reactor 1 is connected on one side to a vacuum
part of the installation by way of a mercury stopper and,
on the other side, by way of mercury stopper 3 to an ex-
tension 4 with crystalline iodine. The extension 5 serves

to create a flow of iodine vapor at a definite pressure, corresponding to the pressure of the medium in which the extension is placed. The entire reactor is placed in a thermostat with a given temperature.

Inside the reactor, a beaker equipped with a glass window (8), -- with a thickness of 0.1 - 0.05 mm. --, was installed by fitting it to the ground neck of the reactor. Inside the beaker, a lead guard (9) was placed -- with a thickness of 3 mm. -- with a corresponding opening facing the glass window. By turning the stopper (12), the guard could be turned in such way as to close the window during measurement of the natural background by the counter 10. Inside the beaker it was possible to create an appropriate vacuum to guard the window from destruction. For avoidance of sorption of water vapors, the surface of the mercury in the stoppers was covered with phosphorus acid. The ground neck of the beaker was also smeared with the same acid.

Iodide marked with radioactive iodine (I^{131}) was placed on the window in the form of a solution and then evaporated at a temperature of 80-90°. The total quantity of iodine in the layer, as a rule, did not exceed 0.1 mg. Thus, self-absorption of β--particles (0.6 mev) could be neglected. The time duration was small (2-3 hrs) in comparison with the period of the half-life of I^{131} (8 days).
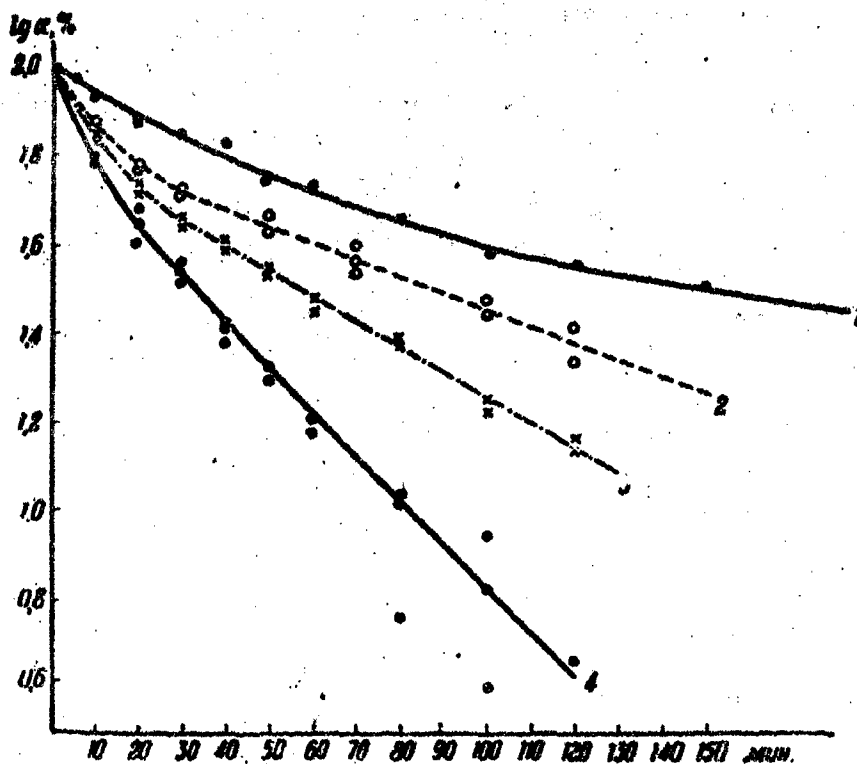
Fig. 2. Relationship between $\lg \alpha (\%)$ and time at $293°K$ for LiI.

After evacuation of the reactor, the stopper 2 was closed and the stopper 3 was opened. Iodine evaporated in the extension 4 and condensed in extension 5. The radioactivity of the iodide layer was measured periodically.

The portion of the unchanged atoms of the radioiodine were determined by a ratio:

$$ a = \frac{A_t}{A_0}, $$

where A_0 — is radioactivity of the layer at the beginning of the experiment,
   A_t — is radioactivity of the layer at the moment of time t.

Fig. 2 indicates the relationship between $\lg \alpha (\%)$ and the time for lithium iodide at various concentrations of iodine in the gaseous phase and at a temperature of $293°K$.

Roentgenographic measurements for the crystals of lithium iodide produced mean statistical measurements of $1.2 \cdot 10^{-4}$ cm.

On the basis of this data, Table 1, containing cal-
culating values for R and D, was compiled.

Table 1

Relationship between R and D and LiJ for LiI at $T = 293°$ K

c mg/cm^3	$z, 10^{-4}$ i/sec	$R, 10^{-4}$ cm/sec	$w, 10^{-4}$ i/sec	z/w	φ	$D, 10^{-11}$ cm^2/sec	Remarks
$1,3 \cdot 10^{-4}$	0,198	0,8	0,124	1,6	1,01	1,7	
$1,65 \cdot 10^{-4}$	0,396	1,6	0,159	2,54	1,30	1,2	
$2,8 \cdot 10^{-4}$	0,693	2,8	0,199	8,48	1,96	1,5	
$2,8 \cdot 10^{-4}$	0,651	2,6	0,189	8,45	1,86	1,4	Layer 10 times thick
$4,0 \cdot 10^{-4}$	1,425	5,7	0,262	5,45	1,48	2,4	

As is evident from the data in the table, the value
of the self-diffusion coefficient remains practically con-
stant while the observed constant of the velocity exchange
on the surface grows with an increase of the iodine concen-
tration in the gas phase.

It is interesting to note that an increase in the
mass of the solid phase by 10 times does not materially
increase the values of R and D. From this observation
it follows that the diffusion velocity of iodine vaopors
in a gas phase does not in the least influence the exchange
velocity, and that the measurements were taking place in
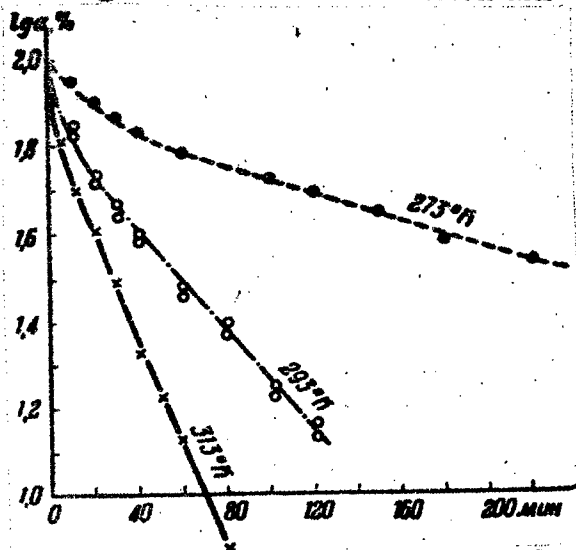the region of kinetics exclusively.

Fig. 3. Relationship
between $\lg \alpha$ (%) and
time at various T.

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The observed reaction velocity constant had the following relationship with the concentration of iodine in the gas phase:

$$R = kc^2,$$

where $k = 44,5 \frac{\text{см}}{\text{сек}} \frac{\text{см}^6}{\text{мг}^2}.$

The finding of a relationship between the velocity of the isotope exchange (k) and the self-diffusion coefficient (D) and the temperature was conducted on the basis of the kinetic curves $\lg \alpha - t$ at 20° to 40°. The values of k and D obtained from these curves (Fig. 3) and their relationship to temperature are given on Fig. 4.

The slope of the straight lines $\lg k - \frac{1}{T}$ and $\lg D - \frac{1}{T}$ corresponds the activating energy

$$E_k = 9900 \text{ cal/mole and } E_D = 9700 \text{ cal/mole.}$$

The isotope exchange of water vapors with other iodides was studied at temperatures of $293^\circ K$ and various concentrations of vapors.

Table 2 presents the values found for k and D.

Table 2

Values of k and D for iodides at $T = 293^\circ K$

Charge of cation	Radius of Cation Å	Iodide	k, $\frac{\text{см}^3}{\text{sec}} \frac{\text{см}^6}{\text{mg}}$	D, см²/sec
1	0,60	LiJ	44,5	$1,7 \cdot 10^{-11}$
1	0,95	NaJ	27,5	$0,062 \cdot 10^{-11}$
1	1,33	KJ	28,0	$0,02 \cdot 10^{-11}$
2	0,99	CaJ$_2$	33,0	$0,14 \cdot 10^{-11}$

From this data it is apparent that the velocity constant of the exchange does not appreciably change while passing over from one cation to another. On the contrary, the self-diffusion coefficient of iodine in the crystal of iodide changes fairly strongly depending on the cation.

At the same time, it decreases with the growth of the radius of the cation and increases with the growth of the charge. This fully agrees with the data regarding almost instantaneous exchange between aluminum iodide and iodine (radius of aluminum ion = 1.57 Å and of the charge 3+).
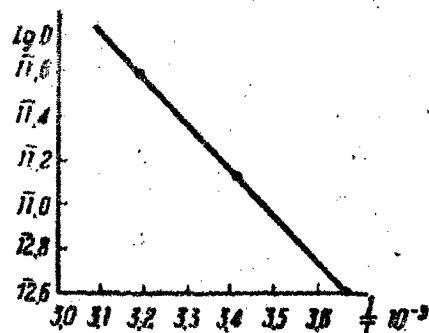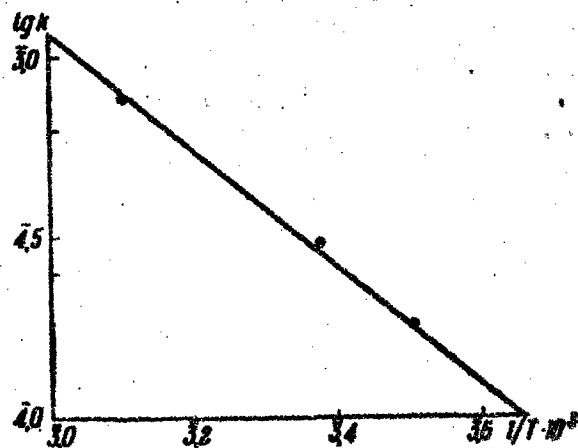
Fig. 4. Relationship between $\lg D$ and $\frac{1}{T}$.

Fig. 5. Relationship between $\lg k$ and $\frac{1}{T}$.

The author expresses his thanks to G. Z. Roginskiy for his valuable suggestions.

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